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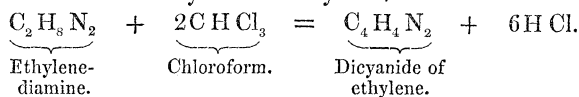
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I have designated the body described in this note by the name of *cyanide of amyl*; I am of course aware that the same name has been given to the substance produced by the action of cyanide of potassium on the sulph-amylates; but as the latter compound, in consequence of its transformation into caproic acid and ammonia, has a right to the name *capronitrile*, I have thought it desirable to distinguish, provisionally at least, the new product by the name of cyanide of amyl.

The examination of the cyanides of amyl and phenyl establishes in a positive manner the existence of a group of bodies isomeric with the nitriles derived from the ordinary alcohols and phenols.

I have not as yet pursued more minutely the study of the other terms of these groups; in fact the field opened by these new observations presents questions much more attractive. The existence of the new homologues of hydrocyanic acid allow us to foresee the formation of quite another series of homologues of cyanogen. These bodies will be produced by the action of chloroform on the diamines. Ethylene-diamine, for example, will thus be transformed into the dicyanide of ethylene;—



I am now occupied with the study of the action of chloroform on ethylene-diamine, and I propose shortly to inform the Royal Society whether experiment confirms the predictions of theory.

III. "On a New Series of Bodies Homologous to Hydrocyanic Acid."—

III. By A. W. HOFMANN, LL.D., F.R.S. Received September 7, 1867.

The new cyanides isomeric with the nitriles, which I have described in two previous communications, are not formed exclusively by the action of chloroform on the primary monamines. On perusing the papers describing the examination of the organic cyanides, we see at a glance that the chemists who investigated them have had in their hands at the same time the isomeric cyanides with which I am engaged.

In fact everyone who has distilled mixtures of sulphomethylate, sulph-ethylate, or sulphamylate of potassium with the cyanide of the same metal, will remember the repulsive odour possessed by the products so obtained. This odour only disappears in proportion as the product is purified, and especially after its treatment with acid, in order to remove the ammonia, and with oxide of mercury to separate the hydrocyanic acid.

Dumas, Malaguti, and Le Blanc, in their researches on the nitriles, mention the insupportable odour possessed by the cyanides obtained by the cyanide-of-potassium process; while the products obtained by the dehydration of the ammoniacal salts by means of phosphoric anhydride have a very agreeable aromatic odour.

In a research made by Mr. Buckton and myself on the transformations of the amides and nitriles under the influence of sulphuric acid, we repeatedly had occasion to prepare acetonitrile (cyanide of methyl) and propionitrile (cyanide of ethyl) by the distillation of a sulphomethylate or sulphethylate with cyanide of potassium. In our paper we mention substances of a formidable odour which appeared in these reactions, and we describe the efforts we made in order to isolate them. But as they are only formed in small quantity, we had to give up the attempt.

Mr. E. Meyer*, who has also been occupied with cyanide of ethyl, but who employed another method of preparation, encountered the same bodies. By acting on cyanide of silver with iodide of ethyl in sealed tubes, he obtained, together with iodide of silver, an unstable compound of cyanide of silver and cyanide of ethyl; and there was formed in the same reaction a liquid of an overwhelming odour. This latter, on distillation, presented the characters of a mixture from which it was impossible to isolate a product with a constant boiling-point. When treated with an acid the odour disappeared, and the solution contained ethylamine which was identified by the analysis of the platinum-salt. These are certainly the characters of the cyanides formed by the action of chloroform on the primary monamines; and it cannot be doubted that Mr. Meyer has had in his hands the ethyl-term of the series of cyanides which I am studying, both in the combination with cyanide of silver and in the complex liquid which accompanied it.

If such results did not particularly attract the attention of chemists, it was owing to the fact that the author failed in ascertaining the complementary product of ethylamine, namely, formic acid. Mr. Meyer, besides, states that his research remained unfinished; and thus it will be understood how experiments otherwise so carefully carried out should have fallen into an oblivion from which neither the author nor any other chemist has endeavoured to recal them during the many years which have elapsed since their publication.

In consequence of the examination of the bodies produced by the action of chloroform on the primary monamines, these old experiments have acquired a new interest; and it appeared to me, for more than one reason, that it would be desirable to repeat them, making use of the experience gained by my late researches.

For this purpose I have submitted cyanide of silver to the action of several organic iodides.

The iodides of methyl and ethyl act very slowly on cyanide of silver at the ordinary temperature; but the reaction takes place at the temperature of boiling water.

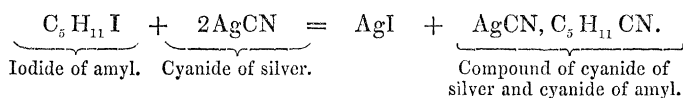
After a digestion of about ten hours, the transformation is complete; a brown solid matter is formed, having the appearance of paracyanogen, together with a yellowish oily layer possessing in a marked manner the odour of the isomers of the nitriles.

* *Journal für praktische Chemie*, vol. lxxvii. p. 147.

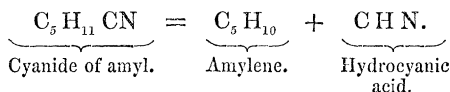
As several preliminary experiments gave indications of a rather complicated reaction, and as it would have been difficult for me readily to obtain sufficient substance by operating in sealed tubes, I performed the experiment in the amylic series, supposing that the higher boiling-point of the iodide of amyl would render it more easy of attack. My expectation was indeed fulfilled: two molecules of cyanide of silver and one molecule of iodide of amyl act on one another with extreme violence at the boiling-point of the latter. It is convenient to operate on a moderate scale, so as to be carefully protected from the escaping gases, which consist of equal volumes of amylene and hydrocyanic acid, mixed with a small quantity of the cyanide of amyl.

The experiment was made in a retort adapted to the lower end of a condenser, the upper end of which was connected with a series of washing-bottles. In the first a small quantity of cyanide of amyl was condensed; the second contained water intended to absorb the hydrocyanic acid; the third one water and bromine in order to transform the amylene into bromide, of which I was thus enabled to collect a considerable quantity during my researches.

After an hour's digestion, the reaction is finished, and the residue in the retort consists of a dark viscous mass, becoming almost solid on cooling; this is a mixture of iodide of silver and a combination of cyanide of silver and cyanide of amyl. The reaction then takes place according to the equation:—



But simultaneously a certain quantity of cyanide of amyl splits into amylene and hydrocyanic acid:—



This secondary transformation depends principally on the manner in which the operation is conducted; it may give rise to very great loss if the reaction be rather tumultuous.

It was now necessary to separate the cyanide of amyl from the residue in the retort. Up to the present time I have found no other means of effecting this than by submitting the residue to dry distillation; in this operation a further quantity of hydrocyanic acid and amylene is disengaged, and a liquid distils over, which on rectification boils between 50° and 200°. By submitting it to fractional distillation it was found that the first part still contained a quantity of amylene, whilst the latter products had become inodorous. The intermediate portion, rectified several times, finally exhibited a constant boiling-point between 135° and 137°.

The liquid which distils at this temperature is perfectly pure cyanide of amyl. It possesses all the properties which I have described in my previous communication, and is characterized especially by its odour and by the facility with which, under the influence of hydrochloric acid, it splits into formic acid and amylamine. I have not yet completely examined the products boiling at a higher temperature, but everything seems to show that they consist, partly at least, of capronitrile.

The experiments which I have just described show, in a positive manner, that the same bodies can be obtained by the action of chloroform on the primary monamines, and by the treatment of cyanide of silver with the alcoholic iodides. In the latter process many secondary products are obtained; but by a more complete study perhaps it may be modified so as to diminish their quantity.

However this may be, the study of the action of the alcoholic iodides upon silver-salts deserves to be resumed; and it is very probable that in many cases it will be found that the bodies so produced will be but isomeric with those obtained by the ordinary processes.

For the special researches in which I am engaged at the present time, the observations just described have a particular interest; they permit us, in fact, to produce the isomeric cyanides without first preparing the primary monamines; they are especially important with reference to the generation of the polycyanides. The polyamines, in fact, are little, if at all, known up to the present, whilst the iodides of methylene and ethylene and iodoform are easy to procure.

If I have not yet succeeded in preparing a dicyanide of ethylene, $C_4H_4N_2$, isomeric with Mr. Maxwell Simpson's cyanide, it is because I have not had at my disposal a sufficient quantity of ethylene-diamine. I now hope to obtain this body by submitting cyanide of silver to the action of iodide of ethylene.

In conclusion, I may be permitted to announce as very probable the existence of a series of bodies isomeric with the sulphocyanides. Already Mr. Cloez has shown that the action of chloride of cyanogen on ethylate of potassium gives rise to the formation of an ethylic cyanate possessing properties absolutely different from those belonging to the cyanate discovered by Mr. Wurtz. On comparing, on the other hand, the properties of the methylic and ethylic sulphocyanides with those of the sulphocyanides of allyl and phenyl, we can scarcely doubt that we have here the representatives of two groups entirely different, and that the terms of the methylic and ethylic series, which correspond to oil of mustard and to the sulphocyanide of phenyl, still remain to be discovered. Experiments with which I am now engaged will show whether these bodies can be obtained by the action of the iodides of methyl and ethyl on sulphocyanide of silver.

I must not conclude this note without expressing my thanks to Messrs. Sell and Pinner for the hearty cooperation that they are giving me in these researches.